Dynamics of Step Doubling: Simulations for a Simple Model and Comparison with Experiment

S.V. Khare, T. L. Einstein, and N.C. Bartelt

Department of Physics
University of Maryland
College Park, MD 20742-4111

To interpret recent experiments on the dynamics of step doubling, we have studied a simple model of this phase transition. With Monte Carlo, we compute the time-dependence of the order parameter in the limit of rapid diffusion across terraces. Analysis of the data shows that the limiting step is the time for adjacent steps to touch each other; subsequent "zipping" together happens rapidly. From this vantage we develop an analytic expression for short times that changes into a phenomenological one for later times. Using data from two physical systems, we compare this function and another based on naive assumptions with a third based on chemical rate theory. For the more recent data, our expression describes the data best. Finally, in the opposite limit in which atoms can only move along step edges, we show characteristic configurations and compute the structure factor.

I. INTRODUCTION

Reversible structural phase transitions on stepped metals and semiconductors have attracted increasing attention over recent years. In particular, there have been several studies of transitions from single- (or monatomic) height to double-height steps. Over two decades ago, Lang *et al.* [1] noted merging of single-height steps on Pt{554} (or $[9(111)\times(11\bar{1})]$) to form double-height steps after exposure to oxygen. (With carbon, the steps tripled!) Thapliyal and Blakely [2] observed stable double-height steps at temperatures below 623K and single-height steps at higher temperatures on Ni{332}, i.e.(111)-10°$[1\bar{1}0]$. They further found that by holding the surface at about 670K, bulk carbon impurities precipitated to the surface, producing facets with {111} and {110} orientations. Evidently the step doubling is produced by carbon changing the surface free energy rather than by an entropy effect. (In contrast, in the simplest picture, as the temperature decreases the extra entropy of single height steps becomes less important than the presumably lower energy of double height steps.) Oxygen exposure was again found to lead to step doubling by Castner and Somorjai [3] for Rh{775} and Haase *et al.* [4] for Ni{771}. Step doubling without any impurity, just as a function of temperature, was reported on vicinal Si{001}-(2×1) by Alerhand *et al.* [5] and on vicinal Ge{111} by Jung *et al.* [6]. Recently, Chang and Blakely [7] also observed step doubling on Ni(111)-5°$[11\bar{2}]$.

It has also been possible to study the *dynamics* of these step-doubling transitions. A decade ago Comsa *et al.* [8] reported the dynamics of the step doubling caused by oxygen on Pt{997}. Recently, there has been renewed interest in this subject. Niu *et al.* have measured the time rate of growth of double-height steps on Ni{977} when exposed to oxygen [9]. Hoogers and King [10] (henceforth referred to as HK) have reported similar measurements on oxygen-induced doubling on Rh{332}.

Little theoretical work has been done to understand the dynamic processes governing these transitions. To gain insight into the key mechanisms, we performed Monte Carlo calculations of a simple model of step-doubling transitions. In computational models, it is easy to prepare a system in an arbitrary configuration and then to study the evolution. This procedure amounts to a thermal quench (or upquench from zero temperature). By examining the results of these simulations, we find that the rate-limiting process is the time it takes for neighboring steps to make contact with each other at some point, due to their meandering. We produce an analytic expression for the evolution of the order parameter based on this perspective. We compare the results with recent experiments. In these experiments the surface is brought quickly into a regime where double-height steps are stabilized by dosage with oxygen, thereby changing essentially the chemical potential rather than the temperature. A major goal in this work is to gain greater insight into the way in which steps diffuse on surfaces, a problem that has been of considerable activity in recent years. Another question is the microscopic role of oxygen in these processes. Our approach will assume that it rather passively changes relative chemical potentials, acting like a thermodynamic field and so analogous to shifting the temperature, rather than participating actively in the diffusion by etching, pinning, etc. The role of these effects, not explicitly included, may well need to be added in future studies. Moreover, in assuming that the doubling arises from a sudden change in a thermodynamic field, we are neglecting kinetic factors such as deposition rates or transport asymmetries over steps [11], which might cause doubling during growth or evaporation.

II. SIMULATION AND RESULTS

Using standard Monte Carlo methods with the Metropolis algorithm, we studied step-doubling dynamics in a terrace-step-kink (TSK) model [12], in which step wandering is the only thermal excitation. We used a two-dimensional square lattice of dimensions $L_x \times L_y$, with screw-periodic boundary conditions in the $\hat{x}$ direction to create four steps. Various values of L_x from 32 to 64 were used, so that the initial uniform interstep separation $\bar{\ell}$ was between 8 and 16. L_y was always chosen to be 80, and periodic boundary conditions were applied in the $\hat{y}$ direction. In recent work we found that these sizes were large enough to show a distinct phase transition [13]. Moreover, the {977} surface, here of Ni, has terraces that are 7 rows wide, the step risers being {100} microfacets (i.e. A steps on the {111} terrace). The {332} surface (of Rh) has terraces 5 rows wide, the step risers being {111} microfacets (i.e. B steps) [14].

The energy of a double-height step per unit length was chosen to be equal to the energy ϵ of a single-height step of same unit length. This *Ansatz* is the simplest way to have energetics favor the pairing of steps. Barring some rather pathological choice of relative kink energies on the two kinds of steps, *entropy* will favor having single-height steps rather than [half as many] double-height steps. Again for simplicity, we set the energy of a [single] kink (or anti-kink) on either kind (single height or double height) of step to have the same energy, ϵ, neglecting corner energies as well as the structural difference between the steps: The goal in this model is to reproduce the relevant physics with the minimum number of parameters. In the TSK approximation, overhangs of one step over another are forbidden, and there are no terrace defects (adatoms or vacancies). We take as our order parameter Ψ the terrace areas at even heights minus the areas at odd heights, normalized by the total area [13]. Hence, in our simulations, if the two pairs of steps each join completely to form two double-height steps, then $|\Psi|$ is precisely unity. We formulate our discussion in terms of unnormalized intensity $I \propto |\Psi|^2$ in order to make contact more readily with measured data. The model was studied under two conditions of the order parameter: a) not conserved, with $-1 \leq \Psi \leq 1$ and b) conserved, with $\Psi = 0$.

In case a, appropriate to evaporation/condensation transport, the system was thought of as being connected to a reservoir of atoms. Each Monte Carlo time step (MCS) consisted of $4L_y$ random selections of sites along steps at which the step was either incremented or decremented by a unit length (at cost 2ϵ for initially straight steps), or left unchanged (i.e. "Glauber dynamics"). This is the so-called evaporation/deposition mode [15]. In the physical system the reservoir would be provided by a two-dimensional "gas" of adatoms and/or vacancies

on the terraces diffusing rapidly compared to the attachment/detachment time. By using a reservoir as the intermediary, we have excluded any asymmetry in attachment of atoms arriving from above or below the step, thereby avoiding a kinetic prejudice of the steps toward or against merging [11]. Note that in the TSK model, there are no adatoms on the terraces. This simplification, which neglects details of the transport of atoms from step to step, greatly aids in acquiring adequate statistics in the Monte Carlo runs.

The equilibrium properties of this model were studied previously by Einstein *et al.* [13]. Consistent with that work, we observed a step-doubling phase transition at a critical temperature $T_c \approx 1.3\epsilon/k_B$, where k_B is Boltzmann's constant. This transition was second-order, in the Ising universality class, reflecting spontaneous breaking of symmetry between even-height and odd-height terraces. If not preempted by a first-order transition, this behavior presumably occurs for the fcc metals Ni and Rh where these step doubling transitions have been observed, as well as on Ge(111) [6,13]. (In contrast, on vicinal Si(001) surfaces miscut towards a [110] direction, there is no spontaneous symmetry breaking between alternate terraces: symmetry has already been broken by the (2×1) reconstruction, which produces dimer rows which run alternatively parallel and perpendicular to the step edges on successive terraces separated by single-height steps [16].)

Starting from an initial configuration with straight, uniformly- spaced, single-height steps (so $\Psi = 0$), we monitored the time dependence of the order parameter for different values of the temperature T. In Fig. 1 we plot the square of the order parameter as a function of the Monte Carlo time for two different temperatures, one above T_c and one below T_c.

In our picture of the dynamics, the rate-determining process in step doubling is the wandering of single-height steps until neighboring steps touch at one point. Once the subsequent doubling is achieved at one point of the pair of steps, they relatively quickly "zip" together. The time evolution of Ψ^2 in a *single* Monte Carlo run is shown in Fig. 2. The steep rise in its value from 0^+ to 1^- supports this physical picture.

As a first guess at a reasonable functional form for $\Psi^2(t)$, we note that the order parameter increases rapidly at the outset and eventually appears to saturate at the equilibrium value associated with the final temperature. (See, however, comments at the end of section 4.) At least qualitatively we can describe this behavior as an exponential approach to the asymptotic limit. Since the rate-determining process is the increasing of meandering until the steps touch somewhere, we naively sought to match the initial growth of the order parameter to the root mean square deviation of the step at early times. When the meandering is produced by the attachment and detachment of adatoms and/or vacancies (rather

than diffusion along the step), this deviation is proportional to the one-fourth power of elapsed time [17]. Then the squared order parameter, and so the intensity, should grow initially as the square root of elapsed time. Combining this crude criterion with the exponential behavior leads to the trial fitting expression

$$I_1(t) = A \left[1 - \exp\left(-\sqrt{t/t_0}\right) \right] \qquad (1)$$

The corresponding fits are included in Fig. 1.

To gain a more fundamental understanding of the doubling process, we studied the distribution of times t_c until the order parameter rose steeply. For a run such as illustrated in Fig. 2, t_c was taken as the time when Ψ^2 reached 0.90. (This high threshold, rather than $\Psi^2 = 1/2$, was chosen to limit inclusion of doubling fluctuations in the data set.) The distribution times t_c obtained from 10^4 runs is displayed in Fig. 3. In the simplest approximation, positions on the step are viewed as random walkers in one dimension (viz. the direction perpendicular to the mean step direction), and contact is made when the walker first travels a distance of order ℓ. In this perspective, our problem is to determine the *first passage* time of an unrestricted walker. Letting $t_1 \equiv \bar{\ell}^2/2D$, where D is the effective diffusion constant of the walker, we can write Feller's [21] expression for the distribution of first-passage times as

$$f(t) = (\frac{t_1}{\pi t})^{1/2} \exp(-t_1/t) \qquad (2)$$

This expression is fit to the Monte Carlo data in Fig. 3 by adjusting the vertical and horizontal "scales" so that the peak of the solid curve coincides with that of the data. We see that this simple viewpoint accounts for the short-time behavior of the data but predicts a slower decay beyond the peak of the distribution. Thus, for long times, the simple picture overestimates the chance that a single-height step can survive without making contact at some point with its neighbor. In this regime, the argument of the exponent in eqn. (2) is large, so that the exponential is essentially unity; thus, $f(t)$ is dominated by the power of t. By comparison with the numerical data, we find t^{-2} provides a reasonable description of the long-time decay of $f(t)$. The dashed curve in Fig. 3 is obtained by using an expression of the form of eqn. (2), but with the exponent of t augmented to 2, again adjusted so that the peak coincides with that of the data. We can then replicate the data by using the dashed curve below the peak and the dotted curve above it, giving a somewhat empirical $\tilde{f}(t)$.

We have skirted the issue of which two steps determine t_c: in our system there are four single-height steps initially. Close examination of configurations during several runs provides evidence that it is the touching of the second pair that is associated with the sharp rise in the order parameter. In retrospect, we found small features related to the merging of the first pair of steps, but this process provides at most a modest amount of ordering which may fade as the steps rearrange themselves. Thus, the characteristic length which enters the equation for t_1 should be larger than ℓ, perhaps tending toward 2ℓ in the limit of many steps. Since we have not attempted to interpret D microscopically, a small change in the characteristic length makes no difference in the present analysis.

If we assume that the steps zip together instantly when they make first contact, we can write down the order parameter immediately using $\Psi_z^2(t) \propto \int_0^t \tilde{f}(t')dt'$. Then using eqn. (3) we see that

$$\Psi_z^2(t) \propto \Gamma(-\frac{1}{2}, t_1/t), \qquad (3)$$

where $\Gamma(a, x)$ is an incomplete gamma function, at small t, while at high t it is proportional to $\Gamma(1, t_3/t)$, where t_3 is a fitting parameter. For simplicity, we switch abruptly between the two functions at the time t_2 at which they intersect, determined implicitly by $\Gamma(-\frac{1}{2}, t_1/t_2) = \Gamma(1, t_3/t_2)$. Hence, the resulting functional form has three adjustable parameters, A, t_1, and t_3:

$$I_z(t) = A \left[\Gamma(-\frac{1}{2}, t_1/t)\Theta(t_2 - t) + \right.$$
$$\left. \Gamma(1, t_3/t)\frac{\Gamma(-\frac{1}{2}, t_1/t_2)}{\Gamma(1, t_3/t_2)}\Theta(t - t_2) \right], \qquad (4)$$

where Θ is the unit step function. We defer, until after comparison with experimental data, a discussion of the implications of the approximations involved in producing this equation.

As a third possibility, we also consider the analytic form proposed by HK [10] in the context of trying to explain their experimental data, to be discussed in the next section, in which the doubling is produced by changing the chemical potential (via oxidation) rather than the temperature (*viz.* quenching). HK's model is based on chemical kinetics rather than a microscopic model: the driving mechanism is similar to the one driving the chemical reaction kinetics of two atomic species in a fluid medium. HK propose the following specific functional form:

$$I_{HK} = A \left[1 - \frac{1}{1 + (t/t_{HK})} \right]^2, \qquad (5)$$

where t_{HK}^{-1} in their discussion is a rate constant. Their derivation focuses on fractional occupancy by Rh atoms of single-height steps, double-height steps, and intermediate sites involved in transport. For each of these three quantities, a differential equation expresses its change in terms of the [average] value of the three; correlations are treated in the simplest approximation that they are products of densities. Implicitly, then, it seems that

steps which are not nearest neighbors could pair. A one-dimensional model, it does not distinguish between two totally dissimilar step configurations that have the same value of Ψ but should evolve in different ways. Since step fluctuations were shown above and in previous work by Bartelt *et al.* [17] to play an important role in how steps interact [18] and how they evolve toward equilibrium [19,20], a one-dimensional model should have some problems accounting for the step-doubling process. In fact, HK do note that at lower temperatures, where mean-field approximations describe the correlations less well, the fit is improved if the exponent in eq. (5) is reduced from 2.

As shown in Fig. 4, all the times in our approximants evidently satisfy the same scaling form:

$$t_i \propto \bar{\ell}^4, i = 0, 1, 2, 3. \tag{6}$$

The proportionality constants, of course, depend on the microscopic process in each case, *e.g.* on the overall rate of attachment or detachment of atoms at the steps for t_0. The exponent 4 of $\bar{\ell}^4$ is consistent with previous results of Bartelt *et al.* [17] for step propagation by exchange with a reservoir.

Note that, in broaching the first-passage-time problem, the *Ansatz* of a random walker in 1-D neglects the important contribution of the step stiffness in reducing the fluctuations. ¿From the definition of $t_1 \equiv \ell^2/2D$, we might expect $t_1 \propto \ell^2$. This power is inconsistent with that of eq. (6). Evidently the stiffness of the steps restrains the fluctuations, leading to the higher power. Ultimately, t_1 is determined by fluctuations not just of isolated positions of the step but of large regions. In any case, we note that in the limit of infinite stiffness, the step problem becomes one-dimensional again, with a characteristic time again $\propto \ell^2$.

The distinctions between the predictions of the three expressions for Ψ^2 are clearest at early times. Because of the key role of thermal fluctuations of the step edges in the evolution toward doubling, the small time behavior (i.e., $t \ll t_0$) is, according to eq. (1), $\Psi_1^2 \propto (t/t_0)^{1/2}$ [17]. On the other hand, according to eq. (3), $\Psi_z^2 \propto t^{3/2} \exp(-t_1/t)$, a much smoother onset. These initial doldrums may be an artifact of the assumption that the steps are uniformly spaced at the outset, so that some time is needed for steps to move close to each other. In an experiment, some close approaches should exist before the quench. Finally, the HK expression gives an intermediate behavior: $\Psi_{HK}^2 \propto (t/t_{HK})^2$ at small t. At the other extreme, Ψ_1^2 approaches saturation like a compressed exponential and Ψ_z^2 like t^{-2}, just like Ψ_{HK}^2.

III. COMPARISON WITH EXPERIMENT

In this section we discuss experimental data by HK [10] and by Niu *et al.* [9], hereafter NKGKS, particularly checking how well the increase of the scattering intensity with time is fit by eq. (1).

Having put the three viewpoints in perspective, we now compare the results. Fig. 5 shows the time evolution of the intensity measured by HK for three different temperatures along with their model fits (to eq. (5)) and the fits obtained from eqs. (1) and (4). The fits from the naive model underlying eq. (1) are marginally better than those of the HK model, while the fits using eq. (4) are evidently poorer. The fits to the other three data sets from Fig. 5 of HK [10] give similar results and hence are not shown here. (Note, however, that the approximant in eq. (4) contains three adjustable parameters, one more than the other two cases; as discussed before eq. (4), t_2 is not free.) In contrast, in Fig. 6 we show a sample trace from unpublished work by NKGKS. Here the situation is reversed. The fit to eq. (4) is best, that to eq. (5) slightly worse, and that to eq. (1) notably worse. Evidently the zipping model gives a better account of Niu *et al.*'s data than of HK's. It is not clear what underlies the difference between the two experimental results. We do note that the vicinal surfaces have different step-riser microstructures ({111} for HK, {100} for NKGKS), and the chemical activities are not the same.

Unfortunately, in the very-early-time regime in which the theoretical predictions differ most clearly, the experimental data may often represent a poorly-controlled situation, since the oxygen does not instantly adsorb to alter the surface energetics. Thus, the experimental data may show slower initial growth than if an "instant quench" were possible, leading to a artificially higher power of t in the best fit to data. In the late-time regime, the experimental approach to saturation may be hindered by various kinds of surface defects.

IV. DISCUSSION

In this section we discuss in greater detail the approximations of the microscopic model, the thermodynamic limit, and the relationship to the decay of one-dimensional profiles.

As implied above, the approximation that the steps are initially straight will give a narrower distribution of first-passage times than occur in reality, where there is a distribution of spacings at equilibrium [22], gaussian if the energetic repulsions between steps are significant, broader (approximately squared cosine) when only entropic repulsions enter, as in the model analyzed in this paper. Thus, at early times the actual order parameter should rise faster than in our approximation. However, we believe that the functional form will not change, just a prefactor, as was found for the autocorrelation function of perpendicular fluctuations of specified points along a step [17,23,24].

In a thermodynamic limit of very wide systems (large L_y), but with fixed mean step spacing, the "instant-zipping" approximation must eventually break down. Even initially, the equilibrium fluctuations of the steps must lead to contact between neighbors at some points along their "world lines." The doubling process becomes a sort of dewetting problem in which segments of pairs of single-height steps shrink away [25]. On lattices of the size used in this study, we have seen no evidence of such a wetting regime, and we do not believe it occurs in the experiments, either.

The treatment of the later time period is obviously rather *ad hoc*. The more rapid decrease than expected from one-dimensional walkers seems to be an indication of the two-dimensional nature of the problem: it would be more difficult for a portion of a step, tied to a long "string," to remain isolated from its counterparts on neighboring steps for exceptionally long times. The difficulty of formulating a simple expression may be a consequence of being in a complicated cross-over regime from the Ising-like step-doubling regime to the wetting regime just mentioned.

The subtleties of this problem are mirrored in the rather similar problem of the decay of one-dimensional profiles below the roughening temperature, i.e. surfaces with an initially periodic variation of the local orientation relative to a facet orientation, in one direction across a surface ($\hat{x}$ in our notation) [with uniformity assumed in the other direction (our $\hat{y}$)]. There has been great activity on this problem, with conflicting results arising from differing perspectives, as nicely summarized by Bonzel and Preuss [26]. The viewpoint closest to that espoused here is proposed by Selke and Duxbury [27,28], who have carried out extensive Monte Carlo simulations on problems in this area. Their observation is that the rate-limiting step in the decay process is the annihilation of adjacent up and down steps near the peak or the trough of the periodic undulations. As in step doubling, there is a characteristic time until these neighboring step and "anti-step" pairs contact each other at some point. Then the area of annihilation must spread, much like the doubled step, although the microscopic features are presumably different.

In one way the profile problem is simpler than the doubling problem. In the former, it is always clear which pair of steps (or, more accurately, step-antistep pairs) are coming together. In the doubling problem there is always the possibility that the "wrong" single steps will touch and zip. The time to anneal away this error would presumably be quite long compared to the time scales studied above. To simplify our analysis, we worked with a system having just four steps, eliminating this sort of event. Our belief is that the time to anneal out doublings inconsistent with the overall ordering will be longer than the time scales involved in the experiments. In other words, we expect the late-time limit

of the order-parameter in the experiments is lower than would be expected from an equilibrium analysis. Further Monte Carlo studies of larger systems are certainly warranted to check this viewpoint.

V. FURTHER SIMULATIONS: HOPPING ONLY ALONG STEP EDGES

In case b, the order parameter remains constant in time: $\Psi = 0$. Each Monte Carlo time step (MCS) consisted of choosing $4L_y$ random sites at which a step was either incremented or decremented by a unit spacing (in $\hat{x}$) or left unchanged, and correspondingly one of its immediate neighboring step sites along the same step was decremented or incremented or left unchanged, respectively. This Kawasaki-like formulation corresponds to the physical situation in which diffusion is only along the step edges and not across terraces. The study of this mechanism was motivated by the work of Poensgen *et al.* [29]. There, too, the steps meander considerably; however, since the order parameter is held fixed, they cannot completely fuse together. This restriction creates a wavy pattern of steps as shown in Fig. 7, for the lower temperature of Fig. 1. Note that this figure is an average over many configurations rather than a snapshot of one. At higher temperatures, such as the upper value of Fig. 1, the [time-averaged] steps are still wavy, but they do not touch each other.

Corresponding to the evident periodicity along the $\hat{y}$ direction in Fig. 7, one expects distinctive features in the Fourier spectra. Specifically, we computed the structure factor $S(k_y)$ given by the formula:

$$S(k) = \left| \sum_{m=1}^{4} \sum_{n=1}^{L_y} d(m,n)(-1)^m \exp((2nk\pi i)/L_y) \right|^2 \quad (7)$$

where $d(m,n)$ is the distance between the step edge at point (m,n) on the lattice and the next step edge at $(m+1,n)$. This $S(k_y)$ is the single-scattering approximation of what one would measure in a high-resolution LEED experiment. The result is displayed in Fig. 8. The arrow indicates the distinctive peak which is the signature of the meander of the steps seen in Fig. 7. On an absolute scale rather than the logarithmic scale used in the plot, this peak would be more pronounced and so readily observable in an experiment. However, it is essentially a finite-size effect in the $\hat{y}$ direction. In an experiment, the peak might indicate defect-free regions of a particular size, or could be produced by pinning centers of some sort. Thus, a direct measurement will generally be needed to understand what produces the peak. Moreover, it could be washed out entirely by a distribution of sizes, so that only real-space images such as Fig. 7 would reveal the conserved order parameter.

VI. CONCLUSIONS

We studied a model of step doubling dynamics which shows a second-order, Ising-like step-doubling transition with temperature. A comparison with a recent kinetic experiment has been done. The results suggest that step fluctuations play a key role in the dynamic evolution of the experimental transitions. Step-doubling, from this perspective, is determined by the statistics of a rare event, the time until meandering adjacent steps make contact with each other, essentially a first-passage time.

No effects of the introduction of adatoms like O_2, which actually causes the doubling in the experiments considered above, have been investigated here. The assumption is that quenching into the step-doubled state by changing temperature (a thermodynamic field) or chemical potential (due to adsorption) should have comparable effects. Unfortunately, in the experiment it is difficult to transform the sample rapidly from clean to adsorbed. Hence, the early-time data, which distinguishes most clearly between the different pictures, may often be affected by the adsorption time scale. It would, thus, be useful to do experiments on several different misorientations of the same substance to check the $\bar{\ell}^4$ scaling of the time constants.

Our work is clearly a modest first step in understanding this rich problem. In many physical systems, there are significant energetic repulsions between steps (in addition to the entropic repulsions stemming from the non-crossing of steps). We have not yet explored how they will alter the results presented above. The later-time analysis is blatantly *ad hoc*; further insight into the underlying mechanism might shed light on the profile problem as well.

Doubling could also be produced by other microscopic mechanisms for which the first-passage time would not be a key concept. For example, instead of lowering the energy of double-height steps relative to single-height steps, oxygen could prefer to adsorb on wide terraces, producing an instability toward step bunching, with step doubling typically the most unstable mode. Analogous behavior was observed on Si during evaporation during DC resistive heating [30]. Thus, it would of considerable interest to gain a more thorough characterization (with, e.g., STM [31]) of the microscopic role of the oxygen adsorption in the experiments.

ACKNOWLEDGEMENTS

[1] B. Lang, R. W. Joyner and G. A. Somorjai, Surf. Sci. 30 (1972) 454.

[2] H. V. Thapliyal and J. M. Blakely, J. Vac. Sci. Technol. 15 (1978) 600.

[3] D. G. Castner and G. A. Somorjai, Surf. Sci. 83 (1979) 60.

[4] O. Haase, R. Koch, M. Borbonus and K. H. Rieder, Phys. Rev. Lett. 190 (1991) 621.

[5] O. L. Alerhand, A. N. Berker, J. D. Joannopoulos, D. Vanderbilt, R. J. Hamers and J. E. Demuth, Phys. Rev. Lett. 64 (1990) 2406.

[6] T. M. Jung, R. J. Phaneuf and E. D. Williams, Surf. Sci. 254 (1991) 235.

[7] J. P. Chang and J. M. Blakely, J. Vac. Sci. Technol. A 10 (1992) 2154.

[8] G. Comsa, G. Mechtersheimer and B. Poelsema, Surf. Sci. 119 (1982) 159.

[9] L. Niu, D. D. Koleske, D.J. Gaspar, S.F. King and S. J. Sibener, unpublished; L. Niu, D. Gaspar, D. D. Koleske and S. J. Sibener, Bull. Am. Phys. Soc. 39 (1994) 602.

[10] G. Hoogers and D. A. King, Surf. Sci. 286 (1993) 306.

[11] R. L. Schwoebel, J. Appl. Phys. 40 (1969) 614.

[12] N. C. Bartelt, T. L. Einstein and E. D. Williams, Surf. Sci. 276 (1992) 308.

[13] T. L. Einstein, T. M. Jung, N. C. Bartelt, E. D. Williams and C. Rottman, J. Vac. Sci. Technol. A 10 (1992) 2600.

[14] D. R. Eisner and T. L. Einstein, Surf. Sci. 286 (1993) L559.

[15] W. W. Mullins, in: Metal Surfaces: Structure, Energetics and Kinetics, W. D. Robertson and N. A. Gjostein, eds. (American Soc. of Metals, Metals Park, Ohio, 1963), p.17.

[16] X. Tong and P. A. Bennett, Phys. Rev. Lett. 67 (1991) 101; J. J. de Miguel, C. E. Aumann, R. Kariotis and M. G. Lagally, Phys. Rev. Lett. 67 (1991) 2830.

[17] N. C. Bartelt, J. L. Goldberg, T. L. Einstein and E. D. Williams, Surf. Sci. 273 (1992) 252.

[18] N. C. Bartelt, T. L. Einstein and E. D. Williams, Surf. Sci. 244 (1990) 149.

[19] N. C. Bartelt, J. L. Goldberg, T. L. Einstein, E. D. Williams, J. C. Heyraud and J.-J. Métois, Phys. Rev B 48 (1993) 15453.

[20] A. Pimpinelli, J. Villain, D. E. Wolf, J.-J. Métois, J. C. Heyraud, I. Elkinani and G. Uimin, Surf. Sci. 295 (1993) 143.

[21] W. Feller, An Introduction to Probability Theory and Its Applications, 2nd ed., vol. 1 (Wiley, New York, 1957).

[22] N. C. Bartelt, T. L. Einstein and E. D. Williams, Surf.

Sci. 240 (1990) L591.

[23] L. Masson, L. Barbier, J. Cousty and B. Salanon, Surf. Sci. 317 (1994) L1115 ; 324 (1995) L378 (E).

[24] N. C. Bartelt and T. L. Einstein, unpublished notes.

[25] M. E. Fisher, J. Stat. Phys. 34 (1984) 667, and priv. comm.

[26] H. P. Bonzel and E. Preuss, Surf. Sci. 336 (1995) 209.

[27] W. Selke and P. M. Duxbury, Z. Phys. B 94 (1994) 311; Acta Phys. Slovaca 44 (1994) 215.

[28] W. Selke and T. Bieker, Surf. Sci. 281 (1993) 163.

[29] M. Poensgen, J. F. Wolf, J. Frohn, M. Giesen and H. Ibach, Surf. Sci. 274 (1992) 430.

[30] S. S. Stoyanov, H. Nakahara and M. Ichikawa, Jpn. J. Appl. Phys., Part 1, 33 (1994) 254.

[31] Cf., e.g., J. S. Ozcomert, W. W. Pai, N. C. Bartelt and J. E. Reutt-Robey, Phys. Rev. Lett. 72 (1994) 258.

FIGURE CAPTIONS

1. Ψ^2 vs. t at temperatures $1.404\epsilon/k_B$ and $0.624\epsilon/k_B$, where ϵ is the energy of a kink or, equivalently, a unit length of step. The dashed-dot line gives the results of Monte Carlo simulations, while the solid line is the best fit to the two-parameter functional form $\Psi^2 = A\left[1 - \exp\left(-\sqrt{t/t_0}\right)\right]$. The dashed line is the best fit to the functional form of eq. (4).

2. Ψ^2 vs. t from a single Monte Carlo run at $T = 0.624\epsilon/k_B$, showing the rapid "zipping together" of neighboring steps once they make contact.

3. Distribution of the times at which the sudden rise in Ψ^2 occurs; an illustration of this rise for a sample run was given in Fig. 2. Solid curve: fit of early-time data to eq. (2); dashed curve: fit of late-time data to the phenomenologically altered eq. (2). The curves cross at t_2.

4. Logarithm of the various time constants t vs. logarithm of the average distance $\bar\ell$ between single height steps (i.e., $1/\tan(\phi)$, where ϕ is the misorientation angle), at $T = 0.624\epsilon/k_B$. The plus signs indicate the values of t_0 obtained by fitting eq. (1) to our simulation results. The corresponding linear fit has a slope $s = 4.36 \pm 0.06$. The asterisks, triangles, and diamonds indicate the values of t_1, t_2, t_3, respectively, obtained by fitting eq.(4) to our simulation data. The corresponding best linear fits are shown. Their respective slopes are 3.37 ± 0.30, 3.62 ± 0.25 and 4.03 ± 0.25. This result and those of Bartelt *et al.* [17] suggest a relation of the form of (6).

5. Time evolution of intensity, $I(t)$, at three different temperatures. HK's experimental data [10] is shown at $T = 441.3K$, $T = 474.4K$, and $T = 507.6K$ in order of increasing intensity. The solid lines are their data. The long dashed line is obtained by fitting eq. (5); their functional form obtained from chemical rate analysis, to the data. The short dashed line is the fit of eq. (1) to the data. The dashed dotted line is obtained by fitting eq. (4) to the data.

6. Fit of preliminary data, indicated by diamonds, from Niu *et al.* [9] for $T = 550K$. Also plotted are fits to the expressions in eq. (1): solid curve; to eq. (5): dashed curve; and to eq. (4): dash-dotted curve.

7. Sample of a long time average of the step structure as viewed from a direction normal to the terraces. This simulation was done at $T = 0.624\epsilon/k_B$, and atoms were only allowed to move along the step edge, implying thereby constant Ψ (0 in this case). The four steps were initially straight and uniformly spaced at a distance $\bar\ell = 8$ apart. To help visualize the configuration, a fifth step is depicted here; it is just the first step, shifted by L_x, as dictated by the screw-periodic boundary conditions.

8. The logarithm of the structure factor $S(k)$ given by eq. (7) vs. k_y, where $\hat y$ is along the mean direction of the steps for simulated data such as depicted in Fig. 7, at $T = 0.624\epsilon/k_B$. The distinct periodicity along the step edges is evident from the satellite peak, indicated by an arrow.